

ELECTRODEPOSITION AND CORROSION PROCESSES

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PREFACE TO THE FIRST EDITION

Electrodeposition and metallic corrosion are two aspects of the same basic phenomenon: both involve the transfer of a metal ion through an energy barrier which exists at the interface between a metal and an electrolyte, and each is often influenced in the same way by surface-active agents adsorbed at that interface. There is, for example, a marked similarity between electropolishing and bright electroplating, between the action of pickling restrainers and of organic brighteners in electrodeposition. Naturally, there are differences in detail, but the similarities are sufficiently well marked to make it worth while stressing the physico-chemical bases on which these various processes rest. There seems, nevertheless, to be no modern book dealing with the kinetics of electrodeposition or corrosion processes which makes clear these similarities and differences at a level suitable for first-degree students. Hence this book.

The first part is devoted to a brief consideration of some fundamental electrochemical ideas in so far as these influence our understanding of the thermodynamics and kinetics of electrodeposition and corrosion. Thus, Chapters 1 and 2 describe the phenomena associated with solvation equilibria and overpotential. There follow two chapters on electrochemical corrosion and passivation, where the consequences of these ideas are worked out in some detail; high temperature atmospheric oxidation and liquid metal corrosion are not considered. Chapter 5 takes account of the crystallographic nature of metals and shows how it is possible to modify the electrode kinetics so as to produce bright surfaces. In particular, some of the basic mechanisms of electrocrystallization are discussed. In Chapter 6 the various methods available for preventing corrosion are classified in such a way as to bring out the underlying principles. And, in the final chapter, a somewhat different approach is adopted in discussing recent theories of stress-corrosion cracking, since this phenomenon embodies an interesting interplay of both electrochemical and metal physical concepts.

There follow two brief appendices, one on the co-ordination chemistry

of complex ions and the other on the elementary physics of metal deformation. The first adopts the molecular orbital approach since it is felt that ligand field concepts might prove confusing at this stage.

The book is aimed largely at second- and final-year students in English universities and polytechnics but, in view of the appendices, may possibly command a wider audience. The main difficulties are likely to be encountered in Chapters 5 and 7. In this latter chapter where the exposition of more or less well-established fact gives way to considerations of a more speculative character, references to various key papers in the literature are more highly concentrated than in earlier parts of the book, particularly at points where the views I have expressed are controversial.

In order to keep the size of the book within bounds I have deliberately refrained from detailed description of processes or experimental techniques. Because the treatment is selective in this way, a short bibliography has been appended at the end of each chapter. Most of the books therein referred to develop the subject in a more detailed manner; however, elementary books providing some of the necessary background are also included. Perhaps the most useful companion books to this volume are Evans' *Introduction to Metallic Corrosion* (Arnold, London, 1963), Uhlig's *Corrosion and Corrosion Control* (Wiley, New York, 1962) and Vagramyan and Solov'eva's *Technology of Electrodeposition* (Draper, London, 1961).

My thanks are due to Dr. U. R. Evans, Dr. H. J. V. Tyrrell, Dr. J. E. O. Mayne, Dr. S. C. Barnes and Professor R. W. K. Honeycombe, each of whom read one or more chapters in manuscript and made many useful suggestions. Needless to say, they bear responsibility neither for errors of fact nor any remaining ambiguities in presentation, and the opinions expressed in this book are necessarily my own. I am also grateful to my wife and the staff of the Van Nostrand Company who, by their forbearance and understanding, have in their various ways eased gestation. Finally, I must acknowledge my indebtedness to Dr. T. P. Hoar who unwittingly started it all.

J.M.W.

Sheffield, England
June, 1964

PREFACE TO THE SECOND EDITION

In this second edition I have expanded and modified the early chapters. These are now more comprehensive and I have corrected a number of errors that crept in unobserved. There are now sections on activity in aqueous solutions, concentration overpotential, ionic currents, Stern polarization conductance and polyelectrode systems; and I have incorporated new developments in our understanding of passivity, film breakdown, electrodeposition stress and structure, inhibitors, bacterial corrosion, electrochemical machining and fracture mechanics. A few minor topics such as differential electrode capacity and the electrochemistry of semiconductors are hardly yet of sufficient importance to warrant inclusion, whilst such matters as corrosion in fused salts and high temperature oxidation are comprehensively treated elsewhere. As in the first edition, I have refrained from descriptions of techniques and processes.

The discerning reader will note that I have brought the sign convention for single potentials more closely into line with accepted thermodynamic practice. More especially I have as far as possible adopted S.I. units throughout. My one departure from this otherwise excellent system is to retain 1 square centimetre as the unit of electrode area. Whilst there are significant changes in Chapters 3, 4 and 6, the most comprehensive amendments are to Chapter 5 on electrodeposition and Chapter 7 (stress-corrosion cracking and corrosion fatigue): indeed, the latter is almost entirely rewritten.

My thanks are due to a number of readers and critics for their kind comments on the first edition. I am also indebted to Dr. R. Brook and Dr. D. R. Gabe for their valuable suggestions relating to parts of the revised material and to the staff of Van Nostrand Reinhold for their continued forbearance and encouragement.

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Sheffield, England
June, 1970

SYMBOLS AND ABBREVIATIONS

SYMBOLS

a	Activity (thermodynamic concentration)
b	Tafel coefficient, Tafel slope ($\partial E/\partial \log i$)
C_P	Specific heat at constant pressure (Ch. 1)
e	Electronic charge
\mathcal{E}	Driving e.m.f. available in a cell
E	Young's modulus
E	Single potential of an electrode
E_b	Film breakdown potential
E_F	Flade (passivation) potential
E_R	Reversible single potential
f	Vibration frequency
F	Faraday's constant (96.5 kC/mol or 96.5 kJ/V mol)
G	Chemical free energy
\tilde{G}	Electrochemical free energy
ΔG^*	Chemical free energy of activation
$\Delta \tilde{G}^*$	Electrochemical free energy of activation
H	Enthalpy
ΣI	Ionization energy
i	Current density
I	Total current ($i \times \text{area}$)
i_0	Exchange current density
k	Boltzmann's constant
K_{corr}	Polarization conductance
K_{I_0}	Critical stress intensity factor for plane strain
m	Concentration in mol per 55 mol water
M	Bulk modulus
N_0	Avogadro's number
N_s	Number of metal atoms per cm ² of surface
n	Number of ligands in activated complex
q	Electrical charge

r	Crack propagation rate
R	Gas constant (8.31 J/mol K , $8.7 \times 10^{-5} \text{ eV/K}$)
R	Electrolytic resistance
S	Entropy
t	Transport number
V_L	Volume/cm ² of Helmholtz double layer
W_M	Solvation energy of ion
z	Valency of metal, number of electronic charges on aquo-cation
Z	Atomic number
α	Proportion of active sites in metal surface
α_M	Electronic work function
β	Symmetry factor
β_n	Stability constant
γ	Surface tension, surface free energy
γ_{\pm}	Mean molal activity coefficient (may be written without subscript)
δ	Diffusion layer thickness
$^{\circ}\Delta^+$	Difference relative to solution
$^+\Delta^{\circ}$	Difference relative to metal
ϵ	Electron(s) (Ch. 1), strain (Ch. 7)
η	Overpotential
κ	Solubility product
λ	Transmission coefficient (generally z/ν)
Δ	Sublimation energy
ν	Stoichiometric number
ρ	Resistivity
σ	Stress
σ_Y	Yield stress
τ	Transition time
ϕ	Inner potential
ψ_1	Potential of metal relative to inner Helmholtz plane
Ω	Nobility

ABBREVIATIONS

HER	Hydrogen evolution reaction
IHP	Inner Helmholtz plane
OHP	Outer Helmholtz plane
NHE	Normal (i.e. standard) hydrogen electrode scale of potentials

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Chapter 1

METALS IN EQUILIBRIUM

1.1 Chemical Free Energy and Activation Energy

The 'energy' of anything denotes its ability to do mechanical work of some kind, just as the energy locked up in dynamite—or for that matter the hydrogen atom—can, under suitable conditions, be released in the form of heat, light and pressure. The total amount of energy which is absorbed or released when the constituent chemical bonds of a compound are forged during its formation is termed the **total heat content** H . If now we try to regain this energy by causing the compound to decompose into its constituent elements *at constant temperature and pressure*, we find that the maximum amount we can obtain for doing useful work is different from H . We call this available or 'free' energy the **chemical free energy** G . The 'hidden' energy which makes up the difference between G and H consists of a 'pattern' or 'ordering' energy which reflects the complexity of the atomic arrangement within the molecules. A very complex pattern possesses a high degree of order: one might equally well say that it has a very low randomness or **entropy** S . Experimentally S may be determined by measuring the specific heat (C_p) over the temperature range 0° to $T^\circ\text{K}$, where T represents the temperature measured on the thermodynamic scale*. The more complex a molecule, the greater the change in specific heat with temperature and the more negative its pattern energy TS . We may thus represent the relationship which obtains at constant pressure and temperature between the total heat content and its various parts by the equation

$$H = G + TS. \quad (1.1)$$

This equation may be rewritten

$$G = H - TS, \quad (1.1a)$$

which shows that the chemical free energy available for doing work contains a 'total heat' term and a 'pattern' term, whose negative sign witnesses to the fact that an increase in complexity (i.e. a decrease in S) leads to an increase in available energy.

$$* S = \int_0^T \frac{C_p}{T} dT.$$

When water boils there is no net change in chemical energy, because a change of physical state such as evaporation does not alter the internal chemical constitution of the water molecules, only their spatial separation and external arrangement. Instead, the heat energy $+\Delta H$ gained by the system at constant pressure, which is the work done in separating the water molecules and dispersing them as steam (ΔH is here the latent heat of evaporation) is exactly compensated by the loss in 'pattern' energy $-T\Delta S$ from the system (ΔS being positive because there is an increase in molecular disorder upon evaporation). Thus, for an isothermal physical change, where two phases (liquid and vapour in this case) are in equilibrium at a temperature $T^\circ\text{K}$,

$$\Delta G = \Delta H - T\Delta S = 0. \quad (1.2)$$

This equation applies equally well to chemical changes. Internal molecular rearrangement will spontaneously take place only if it thereby lowers the chemical free energy of a chemical system. Given sufficient time, the chemical reaction will proceed until the free energy reaches the minimum value possible to that system. *The driving force for both physical and chemical reactions is therefore the chemical free energy, and the net free energy change ΔG for a spontaneously occurring process is negative.*

From the viewpoint of an external observer, the elucidation of all the various stages of a complex chemical reaction may be extremely difficult. So far as the energy of the system is concerned, however, reaction is a straightforward business of surmounting one or more energy humps in a progression from one trough or 'energy well' to the next (Fig. 1.1). There is a net decrease in free energy ΔG of the system. The troughs or energy wells occupied by the various atoms in the various stages of their existence denote metastable states or, in the final state shown, a stable one. That is, if a family of particular atoms in an energy well moves to the right or left it meets with an increasingly unfavourable environment. For example, in the 'initial state', we may suppose that movement to the left corresponds to the atoms in question getting too close to their nearest neighbours in the molecules of which they form part (the potential energy of the system rises because compression of the chemical bonds causes the inner electron shells to deform so that they mutually repel one another). Movement to the right might correspond to stretching the chemical bonds and so tending to disrupt the molecules. The greatest barrier to the progress of the reaction is afforded by the largest energy hump which, applying as it does to a family of atoms in the system, is likely to determine the overall rate of progress of the chemical reaction. The energy which the reacting atoms require for reaction to proceed is the so-called **activation free energy ΔG^*** .

The atoms and molecules in any assembly of atoms and molecules tend to vibrate and move about at all temperatures above the thermodynamic zero of temperature (0°K). As the temperature is progressively raised, this *thermal energy* increases: for example, at room temperature the average energy is about 5 kJ/mol^* and at the melting-point of iron has increased to something like 30 kJ/mol . This may be compared with 6 kJ/mol for the

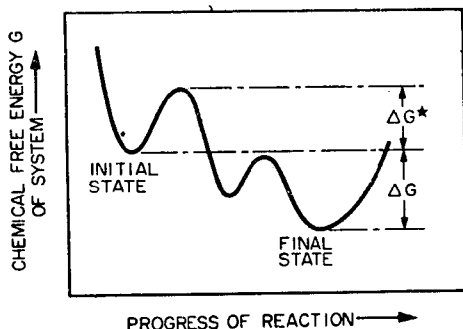


FIG. 1.1 The chemical free energy change of an isolated system in the course of a chemical reaction.

latent heat of melting of ice at 0°C , and 41 kJ/mol for the latent heat of evaporation of water at 100°C . Not all atoms in an assembly have the same energy, some having very much larger values than the average and others much less. Collisions will result in considerable interchange of thermal energy between neighbouring atoms. Boltzmann has shown that, if the total number N of atoms and molecules in the assembly is very large, the number n having an energy equal to or greater than a value E is

$$n = N \exp(-E/kT), \quad (1.3)$$

where k is a constant (Boltzmann's constant) and T the temperature. Because of this distribution of thermal energy between the constituent parts of a chemical system, one can see that the number of atoms or molecules attaining the activation energy ΔG^* necessary for chemical reaction to occur on the lines indicated in Fig. 1.1 will be

$$n = N \exp(-\Delta G^*/kT). \quad (1.4)^\dagger$$

* In terms of the average energy possessed by any one atom this corresponds to 0.05 eV ($= 10^{-20}\text{ J}$).

† Strictly, ΔG^* may only be defined in terms of an equilibrium constant K^* , viz. $n = NK^*$ where n is the activity of the activated complex and N the product of the appropriate activities of the reacting species. ('Activity' is defined in Section 1.3.1 whilst the 'activated complex' is the thermally activated system of atoms and ions constituting the transitional state (Section 2.2).)

1.2 Electrical Potential, Electrical Energy and Electrochemical Free Energy

If some or all of the constituents of a chemical system are electrically charged (i.e. they are ions or electrons), it follows that any attempt to redistribute the charges is going to require the expenditure of work. The work done in taking a unit positive charge from 'infinity', i.e. from any earthed point outside the system to any point in the system is called the **electrical potential** ϕ at that point. In general, every charged particle in the system is characterized by an **electrical energy**; this is equal to the product of its electric charge q and the potential ϕ at the point in space where it is located. It follows that the work required to move an electric charge of q units from one point in the system to another where the electrical potential differs by $\Delta\phi$ is $q\Delta\phi$.

We have seen that every chemical entity possesses chemical free energy G . If any particular entity is electrically charged it will also possess electrical energy $q\phi$, so that the total energy possessed by a charged chemical entity will be

$$\tilde{G} = G + q\phi. \quad (1.5)$$

The quantity \tilde{G} is called the **electrochemical free energy**. For an electrically uncharged chemical substance it will equal the chemical free energy.

As one might expect, the statement made in the previous section, that the driving force in a chemical reaction is the chemical free energy, is true only where no net separation of electrical charges occurs. If the chemical reaction leads to the production or elimination of ions or electrons, the driving force then becomes the *electrochemical free energy: reaction will proceed in such a direction that $\Delta\tilde{G}$ is negative*. At equilibrium, there is no net driving force and $\Delta\tilde{G}$ is zero, just as ΔG is zero in equation (1.2).

1.3 Metal Dissolution

Consider the surface of a metal M contained in a vacuum. Each of the atoms in the metal surface is in fact an ion occupying its own energy well and stabilized in its position by the electron 'gas' in the metal. This 'gas' helps to cement the positive ions together and gives the metal its special properties. If sufficient energy is available (about 600 kJ/mol), it will be possible to pull an ion out of its energy well in the surface, so forming a highly unstable gaseous metal ion M^{z+} which will exert a restoring force on the ion (Fig. 1.2(a)*). However, if the metal is immersed in a polar solvent

* The charge on an electron is here represented by e . The electron itself will be given the symbol e^- . The charge on the positive metal ion of valency z is therefore $+ze$ and that left in the metal $-ze$. For convenience we shall represent the gaseous metal ion by $M^{z+}(g)$ and the equivalent solvated aquo-ion by M_{aq}^{z+} or simply by M^{z+} . Where, in later chapters, it is necessary to refer to complexed ions (e.g. cyano-ions) these will be represented either by $M_{complex}^{z+}$ or written out in full, e.g. $Cu(CN)_3^-$.